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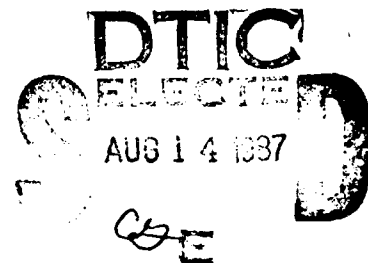# OFFICE OF NAVAL RESEARCH

PROPERTIES AND PHASE TRANSITIONS IN POLYPHOSPHAZENES

Lecture Abstract presented at the Japanese High Polymer Conference

Kyoto, April 27-29 1987, JAPAN

by

J. H. Magill
Department of Materials Science and
Chemical/Petroleum Engineering
University of Pittsburgh
Pittsburgh, PA 15261

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An overview of our work dealing with thermal, physical and related properties of polyphosphazenes of academic and technological interest.

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PROPERTIES AND PHASE TRANSITIONS IN POLYPHOSPHAZENES

J.H Magill

School of Engineering, University of Pittsburgh

Pittsburgh, PA 15261, U.S.A.

Polyphosphazenes were first synthesised towards the end of the last century, but it was not until the mid 1960 that linear polyphosphazenes were prepared [1]. Now, a wide variety of polymers and copolymers with alkoxy, aryloxy and aminoxy groups have been synthesised (see Figure 1). Recently, side chains have been connected directly to the backbone phosphorus modifying physical properties considerably [2]. Variations in side group chemistry enables a wide span in properties to be covered ranging from glass temperatures approaching $-100^{\circ}C$ to melting points well above $300^{\circ}C$ in some systems. Thermotropic behavior persists over a range of temperature from T_m to $T(1)$ depicts the range of this disordered phase seen in Figure 2. Interestingly a useful empirical relationship (Figure 3) has been established [3] involving T_g, $T(1)$ and T_m. The thermotropic range $[T_m-T(1)]$ scales with the side group chemistry for these polymers.

At this point it is appropriate to digress to some practical aspects of these polymers since my polyphosphazene research was first involved with the thermal stability and toxicity of these polymers. The lower toxicity of the degradation products of halogen-free polyphosphazenes (i.e. those closest to D.FIR in Figure 4) proved to be appealing, although it was also realized that specimens with halogen substituents normally raise the oxygen index of polymers generally, which is also desirable [4]. This dichotomy may only be resolved through an appropriate hazard index involving critical parameters for the test evaluation. Analytical and animal testing procedures [5] established

patterns of behavior for polyphosphazenes in relation to other commercial polymers. It was further determined that degradation mechanisms were also important in determining thermal stability. For example, alkoxy phosphazenes degraded primarily via a "chain unzipping" process leaving little or no residue, whereas aryloxyphosphazenes mostly disintegrated through random chain scission (involving some chain transfer too) leaving a substantial residue [6]. Materials that characteristically leave relatively large amounts of intumescent residues (~30 wt % or more) are invariably useful as substrate coatings since heat transfer is curtailed through the creation of such a layer. Poly(aminoxyphosphazenes) are most liable to cross-link creating the largest quantities of char in these polymers. Polyphosphazenes containing additives, have also been studied but exhibited no synergism between additives and polymers[7].

Flammability and flame spread are important commercially but are not well understood. Anyhow, our purpose here was to attempt to establish a useful potential hazard index scale (PHI) for comparing polyphosphazenes with other commercial plastics. Several such relationships have been established empirically [8]. In our case the relation

$$PHI = (W_{max})D_m(\Delta H_c)/(LC_{50}) \; OI \; (T_{max})$$

proved useful where W_{max} is the maximum weight loss over $100°C$ interval, D_m is the smoke density, ΔH_c is the heat of combustion, LC_{50} is the 50% mortality value O.I. is the oxygen index and T_{max} the temperature where maximum weight loss occurs. For comparative testing this relationship showed promise whenever a reference material like Douglas Fir was involved (see Table 1). However, it proved to experimentally demanding because of the many parameters involved.

2

The thermotropic or disordered nature of many polyphosphazenes usually covers a relatively wide range of temperature and imposes a degree of complexity greater than that which exists in semicrystalline homopolymers alone. Before turning to some of these results, it is important to note that short alkyl groups connected directly to the backbone phosphorus destroys thermotropic behavior.

Transitional changes in polyphosphazenes have been studied extensively by thermal techniques. Current investigations are concerned with the coexistence of different morphological forms and phases formed from the melt and from solution. Strikingly, the disappearance of Tg after heat treatment close to or above T_m is accompanied by a substantial increase in sample crystallinity (curve 5 in Figure 5) above 90%, compared to the level found in solution grown crystals (~40%). This behavior is elaborated upon in other papers [9,10] presented at this conference.

X-ray structure diffraction alone has not been very useful in establishing the many polymorphic forms found recently in polyphosphazenes by electron microscopy and diffraction [11,12]. However, physical differences sometimes arise between thin and thick specimens for morphological and other reasons relating to the framework of heat treatment used in sample preparation. For instance, Figure 6 shows the crystal modifications found for poly(bisphenoxyphosphazene)[13]. The lamellar crystals formed from solution (α-form) transform upon heating into a 2D hexagonal δ-form which may be quenched in this disordered state[11]. Only when it is annealed just below T(1) does it crystallize as a 3D hexagonal form - designated as ε-form. However, when the α-form is heated through T(1) (but $<T_m$) and cooled again, it is further stabilized to a λ chain-extended form [14].

Tensile and dynamic mechanical properties also undergo significant changes on passing through the T(1) transition which represents an upper limit to the engineering properties of polyphosphazenes. Figure 7 illustrates the change in dynamic moduli E' (storage) and E" (loss) as well as the significant variation in tan δ at T_g and T(1) respectively[15]. Consistent with these properties is a change in density which is about 6% at each of T(1) and T_m even though the corresponding change in thermal and associated properties is much less[16]. Creep, refractive index and other properties also exhibit transitional behavior.

Another important feature is the kinetics of phase transformations in polyphosphazenes as measured by DSC [17] and X-ray scattering (small and wide angle) techniques[18]. The transformation from the isotropic phase to the 2D form below T_m is too rapid to follow even using synchrotron radiation. However, the isothermal 2D to 3D transition associated with T(1) has been investigated successfully by both methods. The extent of this phase change followed by thermal analysis is dependent upon undercooling. The half-time values (Figure 8) of the transformations are independent of the X-ray scattering technique even though each has inherently different sensitivities. Phase kinetics are internally consistent, and this broad properties approach serves as an overview of our work which will be discussed in more detail in the lecture.

Acknowledgement

References

1. H.R. Allcock and R.L. Kugel, J. Amer. Chem. Soc., 87 4216 (1965).

2. H.R. Allcock, Makrochem. Supp., 4, 3 (1981).

3. M. Kojima and J.H. Magill in "Morphology of Polymers" (B. Sedlacek, Ed.), W. de Gruyter, Berlin/New York (1986).

4. J.H. Magill in Proc. 7th Int. Symp. Flamm. and Fire Retard., N. Orleans, May (1980).

5. K. Sebata, J.H. Magill and Y.C. Alarie, J. Fire and Flammability, 9, 50 (1978).

6. S.V. Peddada and J.H. Magill, Macromolecules, 16, 1258 (1983).

7. S.V. Peddada and J.H. Magill, J. Fire Flammability, 11, 63 (1980).

8. P.J. Lieu, J.H. Magill and Y.C. Alarie, J. Combustion Toxicology, 8, 242 (1981).

9. D.C. Sun, M. Kojima and J.H. Magill, Paper # 1-13-29, this conference.

10. M. Kojima and J.H. Magill, Paper # 1-13-26, this conference.

11. M. Kojima, H. Satake, T. Masuko and J.H. Magill, J. Material Sci. (in press 1986).

12. J.H. Magill, J. Peterman and U. Rieck, Colloid and Polymer Sci., 264, 570 (1986).

13. M. Kojima, W. Kluge and J.H. Magill, Macromolecules, 17, 1421 (1984).

14. M. Kojima and J.H. Magill, Makromol Chem., 186, 649 (1985).

15. I.C. Choy and J.H. Magill, J. Appl. Polymer Sci., 19, 2495 (1981).

16. T. Masuko, K. Simeone, J.H. Magill and D.J. Plazek, Macromolecules, 17, 2857 (1984).

17. D.C. Sun and J.H. Magill, Polymer (to be published 1987).

18. J.H. Magill and C. Riekel, Makromol. Chem. Rapid Comm. 7, 287 (1986).
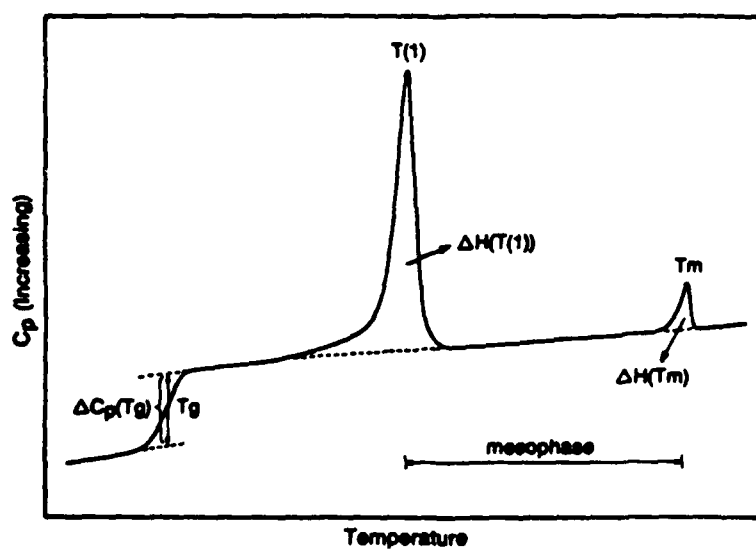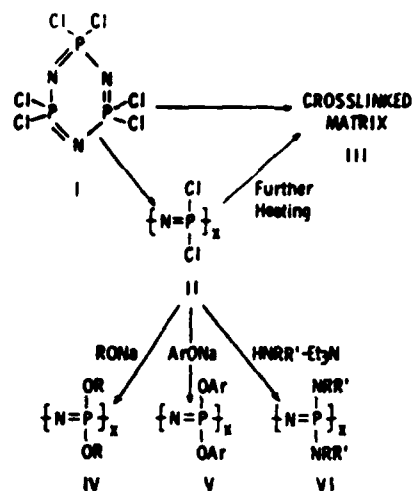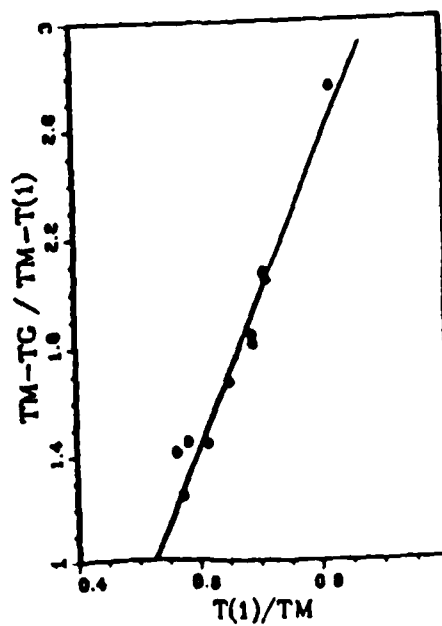
<u>Figure 1</u>

Synthesis
Scheme

<u>Figure 2</u> Transitions in polyphosphazenes
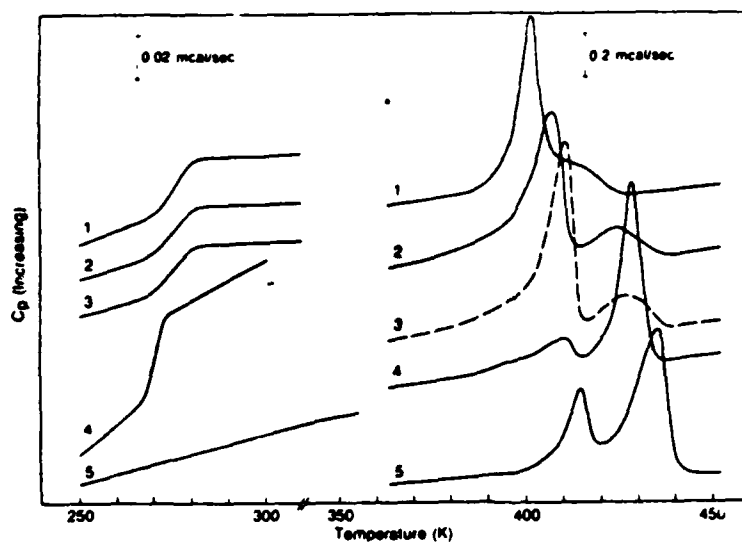
<u>Figure 3</u>
Correlation
between Tg
T(1) and T$_m$

6

Figure 4 LC$_{50}$ values

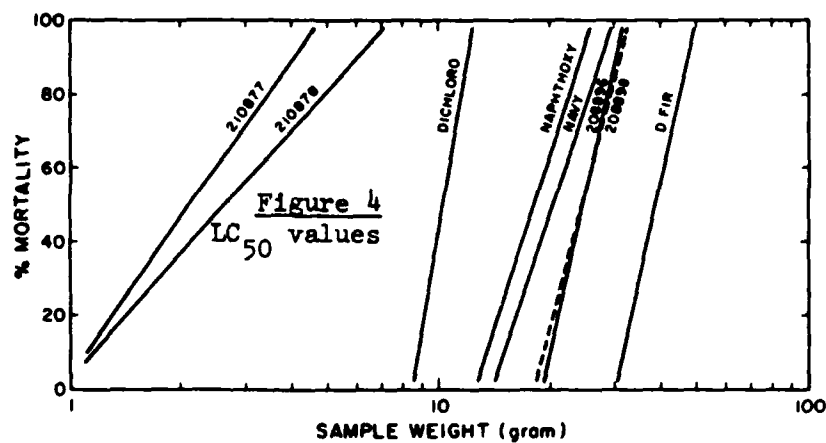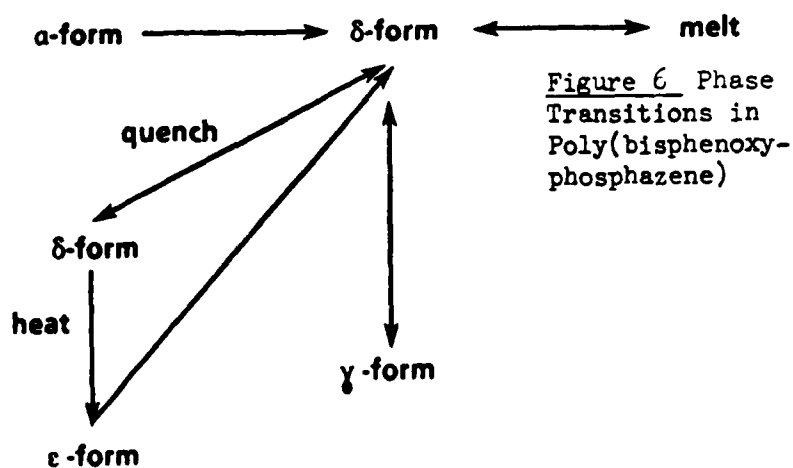Figure 5 Tg and T$_{(1)}$ transitions in Poly(biophenoxy-phosphazene)

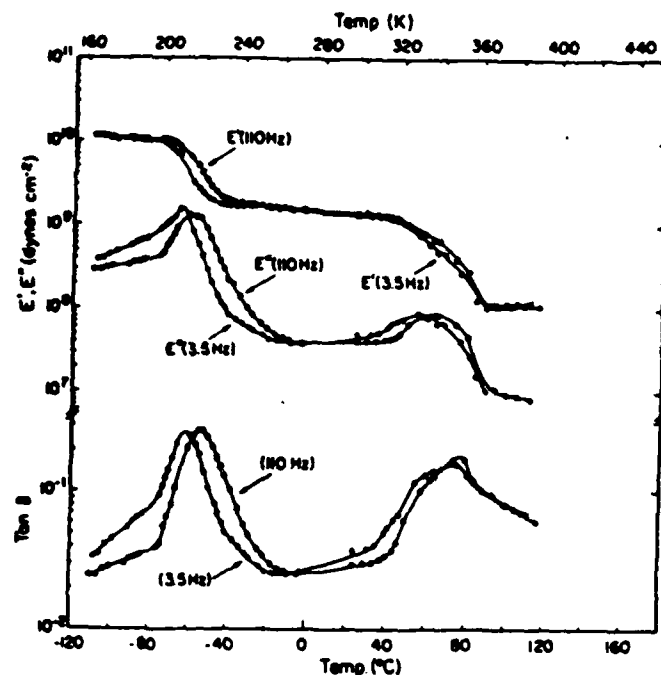Figure 6 Phase Transitions in Poly(bisphenoxy-phosphazene)

7

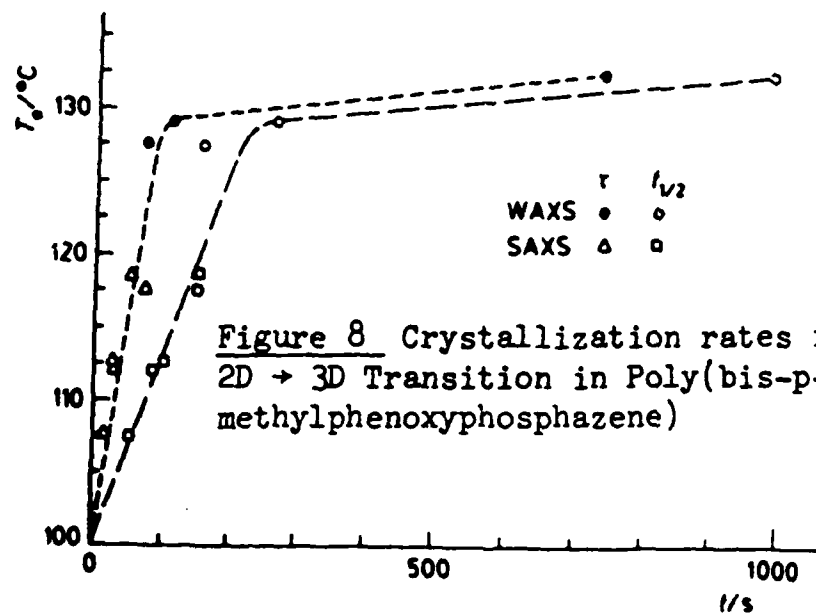Figure 7 Phase Transitions in Poly (bistrifluoroethoxyphosphazene)

Figure 8 Crystallization rates for 2D → 3D Transition in Poly(bis-p-methylphenoxyphosphazene)

MATERIALS DESCRIPTION	OI	ΔH_c (KJ/g)	D_m	T_{max} [f]	V_{max} [b] (%)	LC_{50} (g/m³)	PHI [c]
GM21, flexible polyurethane foam	18	28.2 [e]	204 [e]	713 [3]	74	13.0 [e]	28
GM25, High resilience flexible polyurethane foam	27	26.6 [e]	127 [e]	693 [e]	65	8.3 [e]	17
GM31, rigid polyurethane foam with fire retardants	24	26.4 [e]	775 [e]	593 [a]	30	8.2 [e]	60
APN, polyaryloxyphosphazene [d] foam with $Al_2O_3 \cdot 3H_2O$ and $Mg(OH)_2$	32	28.0 [a]	160	693	15	23.8	2
Douglas Fir	22	19.0	160	623	30	63.7	1

a: estimated value.
b: maximum weight loss over any 100°C interval.
c: value relative to Douglas Fir
d: phenoxy-ethylphenoxycopolymer
e: reference #35
f: sample temperature where maximum weight loss occurs.

Table 1   Potential Hazard Index Values for Selected Polymers

EMD
9-87
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